On Lunn-Senior's Mathematical Model of Isomerism in Organic Chemistry. Part II

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7. Introduction

This paper is a continuation of [3], and we shall use all terminology and notation introduced there.

7.1. Let a molecule's skeleton with d unsatisfied single valences is fixed. Lunn-Senior's thesis 1.5.1 asserts that for any type of isomerism of the molecule with that skeleton (univalent substitution isomerism, stereoisomerism, or structural isomerism) there exists a permutation group $W \leq S_d$ such that each isomer of that type can be identified with a W-orbit in the set T_d, that is, with an element of the set $T_{d;W}$ of W-orbits. If $W = G$, where G is Lunn-Senior's group of substitution isomerism, then the members of the set $T_{d;G}$ represent the corresponding univalent substitution isomers, and the inequalities $a < b$, $a, b \in T_{d;G}$, represent the substitution reactions $b \longrightarrow a$ among them. We denote by G' and G'' the groups of stereoisomerism and structural isomerism, respectively, of the molecule under question. The group G' either coincides with G (there are no chiral pairs), or $G \leq G'$ and $|G' : G| = 2$ (otherwise) — see [7, V] or 1.5.1.

The aim of the paper is to consider a mathematical model in which the following statement from chemistry becomes a well formed formula: the derivatives that correspond to the structural formulae $a, b \in T_{d;G}$ can not be distinguished via substitution reactions. The present approach gives a conceptual basis of the Lunn-Senior's *ad hoc* considerations in [7, VI] (see also 6.4) on the diamers of ethene and of our statements in [5, Sections 3,4,5] concerning the identification of the isomers of certain compounds with one mono-substitution and at least three di-substitution homogeneous derivatives (for instance, benzene and cyclopropane).

It is natural to suppose that a and b are identical as structural isomers, that is, a and b are contained in one and the same G''-orbit, — otherwise they are trivially distinguishable; thus they also have the same empirical formula: $a, b \in T_{\lambda;G}$, $\lambda \in P_d$. Since the substitution reactions are modeled by the inequalities in $T_{d;G}$, and since

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the symmetries are the automorphisms of the corresponding algebraic structure — the partially ordered set $T_{d;G}$ — we define that the products corresponding to a and b are *indistinguishable via substitution reactions* if a and b are identical as structural isomers and if there exists an automorphism $\alpha: T_{d;G} \to T_{d;G}$ of the partially ordered set $T_{d;G}$, such that: (a) $\alpha(T_{\mu;G}) = T_{\mu;G}$ for any $\mu \in P_d$, (b) α maps any chiral pair onto a chiral pair, and (c) $\alpha(a) = b$. Otherwise, they are called *distinguishable via substitution reactions*. The automorphisms α of $T_{d;G}$, which satisfy condition (a) form a group $Aut_0(T_{d;G})$ that acts naturally on the set $T_{d;G}$. The elements $\alpha \in Aut_0(T_{d;G})$ that obey (b) form a subgroup $Aut_0'(T_{d;G}) \leq Aut_0(T_{d;G})$.

In practice, however, the chemists know experimentally enough derivatives as well as enough substitution reactions among them only for a small number of $\lambda \in P_d$ (mono-substitution, di-substitution, tri-substitution homogeneous, etc., derivatives). Thus, we are forced to consider subsets of $T_{d;G}$ consisting of several $T_{\mu;G}$, $\mu \in P_d$, with the induced partial order. For any subset $D \subset P_d$ we define the partially ordered set $T_{D;G} = \cup_{\mu \in D} T_{\mu;G}$ and generalize the above definition in the following natural way: the products corresponding to $a, b \in T_{\lambda;G}$, $\lambda \in D$, are *indistinguishable via substitution reactions among the elements of* $T_{D;G}$ if a and b are identical as structural isomers, and if there exists an automorphism $\alpha: T_{D;G} \to T_{D;G}$ of the partially ordered set $T_{D;G}$, such that (a_D) $\alpha(T_{\mu;G}) = T_{\mu;G}$ for any $\mu \in D$, (b_D) α maps any chiral pair onto a chiral pair, and (c_D) $\alpha(a) = b$. Otherwise, they are said to be *distinguishable via substitution reactions among the elements of* $T_{D;G}$. The automorphisms α of $T_{D;G}$ possessing property (a_D) form a group $Aut_0(T_{D;G})$, and those $\alpha \in Aut_0(T_{D;G})$ which obey (b_D) form a subgroup $Aut_0'(T_{D;G}) \leq Aut_0(T_{D;G})$. The elements of the group $Aut_0'(T_{D;G})$ could be called *chiral automorphisms* of the partially ordered set $T_{D;G}$.

Obviously, if $D \subset D'$, then any automorphism from the group $Aut_0'(T_{D';G})$ induces by restriction an automorphism from the group $Aut_0'(T_{D;G})$, and we obtain a homomorphism of groups $Aut_0'(T_{D';G}) \to Aut_0'(T_{D;G})$. The fact that this homomorphism is, in general, not surjective reflects the plain observation that the products corresponding to $a, b \in T_{\lambda;G}$, $\lambda \in D$, can be indistinguishable via substitution reactions among the elements of $T_{D;G}$, but distinguishable via substitution reactions among the elements of (the wider set) $T_{D';G}$.

7.2. In the beginning of Section 8 we study the relation between the partially ordered sets $T_{d;W}$ and $T_{d;W'}$, for a couple of groups $W \leq W' \leq S_d$ with $|W' : W| = 2$, and the formal behaviour of the group $Aut_0^{W'}(T_{D;W})$ of chiral automorphisms of $T_{d;W}$. Thus, when $W = G$, $W' = G'$ we have $Aut_0^{W'}(T_{D;W}) = Aut_0'(T_{D;W})$, and we generalize the "chiral" situation.

The renumberings of the d unsatisfied valences of the skeleton, which do not affect the group G of symmetries of the molecule, are exactly the elements ν of the normalizer N of G in S_d, and any such renumbering ν induces an automorphism $\hat{\nu} \in Aut_0(T_{D;G})$, $D \subset P_d$. In addition, if $\nu \in N'$, where N' is the intersection of N with the normalizer of G' in S_d, then $\hat{\nu} \in Aut_0'(T_{D;G})$. After A. Kerber (see [6, 1.5]), we call the automorphisms $\hat{\nu}$, where $\nu \in N'$, *hidden symmetries* of the molecule under consideration, or *hidden automorphisms* of the partially ordered set $T_{D;W}$.

In the formal treatment, Theorem 8.2.2 yields $\hat{\nu} \in Aut_0^{W'}(T_{D;W})$, $D \subset P_d$, and, in particular, shows that the hidden symmetries form a subgroup $Aut_0^{h;W'}(T_{D;W})$ of $Aut_0^{W'}(T_{D;W})$, isomorphic to the factor-group N'/W when $(1^d) \in D$. In case $W = G$, $W' = G'$ we denote $Aut_0^{h;W'}(T_{D;W})$ by $Aut_0^h(T_{D;G})$. Under certain condition, chemically

equivalent to existence of chiral pairs among the derivatives with empirical formulae from D, the group $Aut_0^{h;W'}(T_{D;W})$ contains a copy of the factor-group W'/W, generated by the so called *chiral involution* $\hat{\tau}$ that permutes the members of any chiral pair and leaves invariant the diamers (Corollary 8.2.4). In particular, the members of a chiral pair are indistinguishable via substitution reactions, which is the content of Theorem 8.2.6.

On the other hand, the normalizer N acts in a natural way on the set X_W of all one-dimensional characters χ of the group W, $\chi \mapsto \nu\chi$, and this action induces actions of both the factor-group N/W and, under some condition on D, of the group $Aut_0^{h;W'}(T_{D;W})$ of hidden automorphisms, on the set X_W. Given $\theta \in X_{S_\lambda}$, $\lambda \in P_d$, any automorphism $\hat{\nu}$, $\nu \in N$, maps the set of all (χ, θ)-orbits onto the set of all $(\nu\chi, \theta)$-orbits in T_d, and, in particular, any hidden symmetry $\alpha \in Aut_0^{h;W'}(T_{D;W})$ does the same. This is proved in Theorem 9.1.1. As Corollary 9.1.2 we get that any automorphism $\hat{\nu}$, $\nu \in N$, transforms the set of all χ-orbits onto the set of all $\nu\chi$-orbits.

The Extended Lunn-Senior's thesis 1.6.1, hypothesis 5, asserts that for any $\lambda \in P_d$, and for any pair of characters $(\chi, \theta) \in X_W \times X_{S_\lambda}$ the subset $T_{\lambda;\chi,\theta}$ of $T_{\lambda;W}$ represents a type property (χ, θ) of the molecule. Moreover, the automorphism $\hat{\nu}$, $\nu \in N'$, of our algebraic structure transforms the set $T_{\lambda;\chi,\theta}$ onto the set $T_{\lambda;\nu\chi.\theta}$, so the type properties (χ, θ) and $(\nu\chi, \theta)$ are not distinguishable. Thus, it is natural to define that the derivatives which correspond to the structural formulae $a, b \in T_{\lambda;G}$, $\lambda \in P_d$, are *indistinguishable via pairs of characters* if a and b are structurally identical, if for any pair of characters $(\chi, \theta) \in X_G \times X_{S_\lambda}$ with $a \in T_{\lambda;\chi,\theta}$ and $b \notin T_{\lambda;\chi,\theta}$, there exists a $\nu \in N'$ such that $b \in T_{\lambda;\nu\chi,\theta}$ and $a \notin T_{\lambda;\nu\chi,\theta}$, and if for any pair of characters $(\chi, \theta) \in X_G \times X_{S_\lambda}$ with $b \in T_{\lambda;\chi,\theta}$ and $a \notin T_{\lambda;\chi,\theta}$, there exists a $\nu \in N'$ such that $a \in T_{\lambda;\nu\chi,\theta}$ and $b \notin T_{\lambda;\nu\chi,\theta}$. By the specialization $\theta = 1_{S_\lambda}$, we obtain the definition of indistinguishability via characters. Otherwise, these derivatives are called *distinguishable via pairs of characters*, respectively, *via characters*. The central results here are Theorem 9.2.1 and Corollary 9.2.2, which assert that the members of a chiral pair are indistinguishable via pairs of characters and via characters.

In Section 10 we illustrate these ideas by several molecules: those ethene C_2H_4, benzene C_6H_6, and cyclopropane C_3H_6. The results on the last two are valid in a more general situation described in [5]. Since there are no chiral pairs among the derivatives of ethene, its group of "chiral" automorphisms is relatively big — it is described in Theorem 10.1.1. In Proposition 10.1.2 the group of the hidden symmetries of ethene is described. Corollary 10.1.3 gives a rigorous treatment of Lunn-Senior's considerations in [7, VI], concerning the indistiguishability of the diameric pairs $\{a_{(2^2)}, b_{(2^2)}\}$, $\{a_{(2,1^2)}, b_{(2,1^2)}\}$ of ethene. Proposition 10.1.4 and Corollary 10.1.5 specify their indistiguishability via (pairs of) characters, mentioned in 6.4. The group of chiral automorphisms $Aut'_0(T_{D;G})$ of benzene for $D = \{(4,2), (3^2)\}$ is the unit group, so we get once again that the Körner relations identify completely the $(4,2)$- and (3^2)-derivatives of benzene — see Theorem 10.2.1 and Corollary 10.2.2. Theorem 10.3.5 asserts that the group of chiral automorphisms $Aut'_0(T_{D;G})$ of cyclopropane for $D = \{(6), (5,1), (4,2), (4,1^2), (3^2)\}$ is direct product of two cyclic groups of order 2. Corollary 10.3.6 yields that for this D all chiral pairs and all diamers are pairwise distinguishable via substitution reactions.

8. Automorphisms

8.1. Let $W \leq S_d$ be a permutation group. We set $T_D = \cup_{\mu \in D} T_\mu$, $T_{D;W} = \cup_{\mu \in D} T_{\mu;W}$, and consider the partial order on $T_{D;W}$, induced from $T_{d;W}$. By definition, a map

$u: T_{D;W} \to T_{D;W}$ is an automorphism of the partially ordered set $T_{D;W}$ if u is a bijection, and if the inequality $u(a) \leq u(b)$ is equivalent to the inequality $a \leq b$ for any pair $a, b \in T_{D;W}$ (see [1, 3.5]). We denote by $Aut_0(T_{D;W})$ the group of automorphisms of the partially ordered set $T_{D;W}$, such that $\alpha(T_{\mu;W}) = T_{\mu;W}$ for any $\mu \in D$. In particular, when $D = P_d$, we obtain the group $Aut_0(T_{d;W})$.
Let $W \leq W' \leq S_d$ be a pair of permutations groups such that $|W' : W| = 2$. In particular, W is a normal subgroup of W' and the factor-group W'/W has order 2. We denote by χ_e the one-dimensional complex-valued character of W' with kernel W (cf. 6.2). In keeping with 6.2, for any $\lambda \in P_d$ the subset $T_{\lambda;\chi_e} \subset T_{\lambda;W'}$ consists of those W'-orbits in T_λ which contain two W-orbits. Let us set $T_{D;\chi_e} = \cup_{\mu \in D} T_{\mu;\chi_e}$. We fix a $\tau \in W' \backslash W$, so $\tau^2 \in W$. Then we have $W'/W = \langle \bar{\tau} \rangle$, where $\bar{\tau} = \tau W$. The factor-group W'/W acts on the set $T_{d;W}$ via the rule $(\eta W) O_W(A) = O_W(\eta A)$.
We remind that for any $W \leq S_d$ the canonical projection $T_d \to T_{d;W}$ is denoted by ψ_W (see 4.1); its restriction on T_D is the canonical projection $\psi_{D;W}: T_D \to T_{D;W}$. The following technical lemma is obvious.

LEMMA 8.1.1. *Let $D \subset P_d$.*
(i) The surjective map

$$\psi_D: T_{D;W} \to T_{D;W'}, \ O_W(A) \mapsto O_{W'}(A),$$

where $A \in T_D$, is the unique map such that $\psi_D \psi_{D;W} = \psi_{D;W'}$;
(ii) the canonical map

$$(W'/W) \backslash T_{D;W} \to T_{D;W'}, \ O_{W'/W}(O_W(A)) \mapsto \cup_{\eta \in W'} (\eta W) O_W(A)$$

is a bijection;
(iii) after the identification of the orbit space $(W'/W) \backslash T_{D;W}$ with $T_{D;W'}$ via the canonical bijection from (ii), the map ψ_D coincides with the canonical projection $T_{D;W} \to (W'/W) \backslash T_{D;W}$;
(iv) for $a' \in T_{D;W'}$ one has $\#\psi_D^{-1}(a') = 2$ if $a' \in T_{D;\chi_e}$ and $\#\psi_D^{-1}(a') = 1$ if $a' \in T_{D;W'} \backslash T_{D;\chi_e}$;
(v) for any W'/W-invariant map $\alpha: T_{D;W} \to T_{D;W}$ there is a unique map $\alpha': T_{D;W'} \to T_{D;W'}$, such that $\alpha' \psi_D = \psi_D \alpha$;
(vi) for any two W'/W-invariant maps $\alpha: T_{D;W} \to T_{D;W}$ and $\beta: T_{D;W} \to T_{D;W}$, one has $(\alpha\beta)' = \alpha' \beta'$.

We denote by $Aut_0^{W'}(T_{D;W})$ the subgroup of $Aut_0(T_{D;W})$ consisting of the W'/W-invariant automorphisms α, that is, $\alpha(\iota a) = \iota \alpha(a)$ for any $\iota \in W'/W$ and for any $a \in T_{D;W}$.
The lemma below shows, that here we use correctly the notation $Aut_0^{W'}(T_{D;W})$ for the group of chiral automorphisms introduced in Section 7.

LEMMA 8.1.2. *Let $\alpha \in Aut_0(T_{D;W})$. The following three statements are equivalent:*
(i) one has $\alpha \in Aut_0^{W'}(T_{D;W})$;
(ii) there exists an automorphism $\alpha' \in Aut_0(T_{D;W'})$, such that $\psi_D \alpha = \alpha' \psi_D$.
(iii) for any $a' \in T_{D;\chi_e}$ with $\psi^{-1}(a') = \{a, a_1\}$, $a \neq a_1$, there exists $a'' \in T_{D;\chi_e}$ such that $\psi_D^{-1}(a'') = \{\alpha(a), \alpha(a_1)\}$;

PROOF: (i) implies (ii). In compliance with Lemma 8.1.1, (v), any W'/W-invariant map $\alpha: T_{D;W} \to T_{D;W}$ produces a unique map $\alpha': T_{D;W'} \to T_{D;W'}$, such that $\alpha' \psi_D =$

$\psi_D\alpha$. The functoriality of this dependence (Lemma 8.1.1, (vi)) implies that since α is a bijection, then α' is a bijection. Now, we shall show that $\alpha' \in Aut_0(T_{D;W'})$. Obviously, $\alpha'(T_{\mu;W'}) = T_{\mu;W'}$ for all $\mu \in P_d$. Suppose that $a' \leq \bar{a}'$ in $T_{D;W'}$. Equivalently, there are $a, \bar{a} \in T_{D;W}$ such that $a \subset a'$, $\bar{a} \subset \bar{a}'$, and $a \leq \bar{a}$. The last inequality s equivalent to $\alpha(a) \leq \alpha(\bar{a})$, and since $\alpha(a) \subset \alpha'(a')$, $\alpha(\bar{a}) \subset \alpha'(\bar{a}')$, we obtain $\alpha'(a') \leq \alpha'(\bar{a}')$. Conversely, the definition of α' and the previous inequality imply the existence of $a, \bar{a} \in T_{D;W}$ such that $\alpha(a) \leq \alpha(\bar{a})$. Hence the two inequalities $\alpha'(a') \leq \alpha'(\bar{a}')$ and $a' \leq \bar{a}'$ are equivalent.

(ii) implies (iii). Suppose that $a' \in T_{D;\chi_e}$. Then we have $\psi_D^{-1}(a') = \{a, a_1\}$, where $a \neq a_1$. We set $a'' = \alpha'(a')$. Thus, $a'' = \alpha'(\psi_D(a)) = \psi_D(\alpha(a))$, and, by analogy, $a'' = \psi_D(\alpha(a_1))$, so $\psi_D^{-1}(a'') = \{\alpha(a), \alpha(a_1)\}$. In particular, $a'' \in T_{D;\chi_e}$.

(iii) implies (i). Suppose that (iii) holds. Then α maps the set $\psi_D^{-1}(T_{D;\chi_e})$ and its complement onto themselves. We want to show that $\alpha(\iota a) = \iota\alpha(a)$ for any $\iota \in W'/W$ and for any $a \in T_{D;W}$. If ι is the unit element of W'/W, our equality is trivial. Now, let $\iota = \bar{\tau}$. If $a \neq \bar{\tau}a$, then $\psi_D^{-1}(a') = \{a, \bar{\tau}a\}$, where $a' = \psi_D(a)$. Therefore $\psi_D^{-1}(a'') = \{\alpha(a), \alpha(\bar{\tau}a)\}$, and hence $\alpha(\bar{\tau}a) = \bar{\tau}\alpha(a)$. If $a = \bar{\tau}a$, then $\bar{\tau}\alpha(a) = \alpha(a)$, and we have again $\alpha(\bar{\tau}a) = \bar{\tau}\alpha(a)$.

8.2. We remind that via the rule (1.1.1) any permutation $\zeta \in S_d$ induces a bijection $\zeta\colon T_d \to T_d$, $A \mapsto \zeta A$, of the set of all tabloids with d nodes, and its restriction on T_μ is a bijection of T_μ onto itself for all $\mu \in P_d$.

Let $W \leq W' \leq S_d$ be a pair of permutation groups such that $|W' : W| = 2$. We denote by N the normalizer of the group W in S_d, and by N' the intersection of N with the normalizer of W' in S_d. Plainly, $W' \leq N'$.

LEMMA 8.2.1. *For any $\nu \in N$ the bijection ν can be factored out to a bijection $\hat{\nu}\colon T_{d;W} \to T_{d;W}$, $a \mapsto \hat{\nu}(a)$: if $A \in a$, then $\hat{\nu}(a)$ is the W-orbit of νA. Moreover, the bijection $\hat{\nu}$ maps the set $T_{\lambda;W}$ onto itself for any $\lambda \in P_d$.*

PROOF: Given $\nu \in N$ and $\sigma \in W$, there exists $\sigma_1 \in W$, such that $\nu\sigma = \sigma_1\nu$. Therefore $O_W(\nu\sigma A) = O_W(\sigma_1\nu A) = O_W(\nu A)$, so the rule in the condition yields a map $\hat{\nu}$. We have $(\hat{\nu})^{-1} = \widehat{\nu^{-1}}$, hence $\hat{\nu}$ is a bijection of $T_{d;W}$ onto itself, and plainly any set $T_{\lambda;W}$ is $\hat{\nu}$-stable.

THEOREM 8.2.2. *(i) Given $\nu \in N$ and $D \subset P_d$, the bijection $\hat{\nu}$ induces an automorphism from $Aut_0(T_{D;W})$;*
(ii) the map $\nu \mapsto \hat{\nu}$ is a homomorphism of the group N into the group $Aut_0(T_{D;W})$, whose kernel contains W; if $(1^d) \in D$, then its kernel coincides with W;
(iii) the map $\nu \mapsto \hat{\nu}$ is a homomorphism of the group N' into the group $Aut_0^{W'}(T_{D;W})$, whose kernel contains W; if $(1^d) \in D$, then its kernel coincides with W.

PROOF: (i) According to Lemma 8.2.1, $\hat{\nu}$ induces a bijection of the set $T_{D;W}$ onto itself. Let $a, b \in T_{D;W}$, and $A \in a$, $B \in b$. The inequality $a \leq b$ means that there exists a $\sigma \in W$, such that $\sigma A \leq B$, or, equivalently, $\nu\sigma A \leq \nu B$. The inequality $\hat{\nu}(a) \leq \hat{\nu}(b)$ means that there exists a $\sigma_1 \in W$, such that $\sigma_1\nu A \leq \nu B$. Since $\nu W = W\nu$, the last two conditions are equivalent.

(ii) Let $\nu_1, \nu_2 \in N$, and let $a \in T_{D;W}$, $a = O_W(A)$. We have

$$\widehat{\nu_1\nu_2}(a) = O_W(\nu_1\nu_2 A) = O_W(\nu_1(\nu_2 A)) = \hat{\nu}_1(O_W(\nu_2 A)) = \hat{\nu}_1(\hat{\nu}_2(a)) = (\hat{\nu}_1\hat{\nu}_2)(a),$$

so $\widehat{\nu_1\nu_2} = \hat{\nu}_1\hat{\nu}_2$.

Plainly, if $\sigma \in W$, then $\hat{\sigma}(a) = a$ for any $a \in T_{D;W}$, hence W is a subgroup of the kernel. Now, suppose $(1^d) \in D$, and let $\nu \in N$ be such that $\hat{\nu}(a) = a$ for any $a \in T_{D;W}$. The last condition can also be written as $O_W(\nu A) = O_W(A)$ for any $A \in T_D$. In other words, for any $A = (A_1, A_2, \ldots) \in T_D$ there exists a $\sigma \in W$ such that $\nu A = \sigma A$, that is, $\nu(A_1) = \sigma(A_1)$, $\nu(A_2) = \sigma(A_2), \ldots$. In particular, if $A = (A_1, A_2, \ldots, A_d)$ with $A_1 = \{1\}, A_2 = \{2\}, \ldots, A_d = \{d\}$, then $\nu = \sigma \in W$.
(iii) Part (i) applied for the group W' yields that any $\nu \in N'$ induces an automorphism $\hat{\nu}' \in Aut_0(T_{D;W'})$. It is obvious that $\psi_D \hat{\nu} = \hat{\nu}' \psi_D$. Then Lemma 8.1.2 implies $\hat{\nu} \in Aut_0^{W'}(T_{D;W})$. Now, since N' is a subgroup of N that contains W, part (ii) finishes the proof.

Theorem 8.2.2, (ii), yields information concerning the subgroup $Aut_0^{h;W'}(T_{D;W})$ of the group $Aut_0^{W'}(T_{D;W})$, consisting of all hidden symmetries.

Corollary 8.2.3. *If $(1^d) \in D$, then there exists a natural embedding of the factor-group N'/W into the group $Aut_0^{W'}(T_{D;W})$ with image $Aut_0^{h;W'}(T_{D;W})$.*

We set $D_e = \varphi'_W(T_{d;\chi_e})$, where $\varphi'_W : T_{d;W'} \to P_d$ is the restriction of the projection defined in the beginning of Subsection 4.1. Theorem 5.3.1 yields immediately that the subset $D_e \subset P_d$ is an order ideal (see [1, Section 2]) of the partially ordered set P_d. Moreover, $D_e \neq \emptyset$ because at least $T_{(1^d);W'} \subset T_{d;\chi_e}$.

Corollary 8.2.4. *For any $D \subset P_d$ there exists a natural homomorphism of the factor-group $W'/W = \langle \bar{\tau} \rangle$ into the group $Aut_0^{W'}(T_{D;W})$ with image $\langle \hat{\tau} \rangle$. Given $a' \in T_{D;W'}$, the automorphism $\hat{\tau} \in Aut_0^{W'}(T_{D;W})$ maps the fiber $\psi^{-1}(a')$ onto itself in the following way: if $a' \in T_{D;W'} \backslash T_{D;\chi_e}$, then $\psi^{-1}(a') = \{a\}$ and $\hat{\tau}(a) = a$, and if $a' \in T_{D;\chi_e}$, then $\psi^{-1}(a') = \{a, a_1\}$ and $\hat{\tau}(a) = a_1$, $\hat{\tau}(a_1) = a$. If $D \cap D_e = \emptyset$, then $\hat{\tau}$ is the identity. If $D \cap D_e \neq \emptyset$, then $\hat{\tau}$ is an involution and the above homomorphism is an embedding $W'/W \simeq \langle \hat{\tau} \rangle \leq Aut_0^{h;W'}(T_{D;W})$.*

Proof: Because of $W' \leq N'$, the homomorphism from Theorem 8.2.2, (iii), induces a homomorphism $W'/W \to Aut_0^{W'}(T_{D;W})$, $\bar{\eta} \mapsto \hat{\eta}$, where $\bar{\eta} = \eta W$, $\eta \in W'$. In particular, since $\bar{\eta} a = \hat{\eta}(a)$ for any $a \in T_{d;W}$, $\eta \in W'$, Lemma 8.1.1, (iv), yields the prescribed action on the fibers of ψ. If $D \cap D_e = \emptyset$, then for all $a' \in T_{D;W'}$ the fiber $\psi^{-1}(a')$ consist of one inverse image a: $\psi^{-1}(a') = \{a\}$, and this yields $\hat{\tau}(a) = a$, so $\hat{\tau}$ is the identity automorphism. The condition $D \cap D_e \neq \emptyset$ implies that there exists at least one $a' \in T_{D;W'}$ with two inverse images: $\psi^{-1}(a') = \{a, a_1\}$. Then $\hat{\tau}(a) = a_1$, $\hat{\tau}(a_1) = a$, and as a consequence the automorphism $\hat{\tau}$ is an involution. Therefore we get the desired embedding.

In accord with Lemma 8.1.1, (v), and Lemma 8.1.2, for any $\alpha \in Aut_0^{W'}(T_{d;W})$ there exists a unique automorphism $\alpha' \in Aut_0(T_{d;W'})$, such that $\psi\alpha = \alpha'\psi$.

Proposition 8.2.5. *For any $D \subset P_d$ the map*

$$Aut_0^{W'}(T_{D;W}) \to Aut_0(T_{D;W'}),\ \alpha \mapsto \alpha',$$

is a homomorphism of groups and the group $\langle \hat{\tau} \rangle$ is contained in its kernel.

Proof: Let $\alpha, \beta \in Aut_0^{W'}(T_{D;W})$. Lemma 8.1.1, (vi), yields $(\alpha\beta)' = \alpha'\beta'$. Moreover, $(\hat{\tau})'$ is the identity.

The elements of the group $Aut_0^{W'}(T_{D;W})$ are called *chiral automorphisms* of the partially ordered set $T_{D;W}$. In case $D \cap D_e \neq \emptyset$ the involution $\hat{\tau} \in Aut_0^{W'}(T_{D;W})$ is said to be the *chiral involution* of the group $Aut_0^{W'}(T_{D;W})$.
When $W = G$ and $W' = G'$, where G and G' are the groups of substitution isomerism and stereoisomerism, respectively, of the molecule under consideration, and when a distribution of ligants amounts to a chiral molecule, then in compliance with (1.5.1), (2a), we have $|G' : G| = 2$ and denote the group $Aut_0^{G'}(T_{D;G})$ by $Aut_0'(T_{D;G})$.
Taking into account Lunn-Senior's thesis 1.5.1, (2b), we can reformulate (8.2.4) in the following way:

THEOREM 8.2.6. *The members of a chiral pair are indistinguishable via substitution reactions.*

9. CHARACTERS

9.1. Here we continue to use notations, introduced in Section 8. Let X_W be the Abelian group of the one-dimensional characters of the group W. The normalizer N of W in S_d acts on X_W by the rule

$$(\nu\chi)(\sigma) = \chi(\nu^{-1}\sigma\nu),$$

where $\chi \in X_W$, $\sigma \in W$, $\nu \in N$. Since $\sigma\chi = \chi$ for each $\sigma \in W$, we obtain an action of the factor-group N/W on X_W, defined by the rule

$$(\nu W\chi)(\sigma) = \chi(\nu^{-1}\sigma\nu),$$

where $\chi \in X_W$, $\nu \in N$. In particular, since N'/W is a subgroup of N/W, and because of Corollary 8.2.3, in case $(1^d) \in D$ we obtain an action of the group $Aut_0^{h;W'}(T_{D;W})$ of hidden symmetries on the set X_W:

$$(\alpha\chi)(\sigma) = \chi(\nu^{-1}\sigma\nu),$$

where $\chi \in X_W$, $\alpha \in Aut_0^{h;W'}(T_{D;W})$, $\alpha = \hat{\nu}$, $\nu \in N'$.
Now, we refer to the notations from Subsection 5.1. Let λ be a partition of the number d and let θ be a one-dimensional character of the group S_λ. Let $\chi \in X_W$. Given a tabloid $A = \upsilon I \in T_\lambda$, we note that the one-dimensional character β_υ of the stabilizer W_A from (5.1.2) depends only on A, and on χ when θ is fixed, so we introduce the more precise notation $\beta_\upsilon = \beta_{A,\chi}$.

THEOREM 9.1.1. *Given $\nu \in N$, $\lambda \in P_d$, $\chi \in X_W$, $\theta \in X_{S_\lambda}$, one has:*
(i) the automorphism $\hat{\nu}$ of the partially ordered set $T_{d;W}$ maps the set $T_{\lambda;\chi,\theta}$ of all (χ,θ)-orbits onto the set $T_{\lambda;\nu\chi,\theta}$ of all $(\nu\chi,\theta)$-orbits;
(ii) if $(1^d) \in D$, the hidden automorphism $\alpha \in Aut_0^{h;W'}(T_{D;W})$ of the partially ordered set $T_{D;W}$ maps the set $T_{\lambda;\chi,\theta}$ of all (χ,θ)-orbits in $T_{D;W}$ onto the set $T_{\lambda;\alpha\chi,\theta}$ of all $(\alpha\chi,\theta)$-orbits in $T_{D;W}$.

PROOF: Obviously part (ii) is a consequence of part (i).
(i) Let $a \in T_{\lambda;\chi,\theta}$, and let $A \in a$, $A = \upsilon I$. For any $\nu \in N$ we have $\nu A = \nu\upsilon I$, $W_{\nu A} = \nu W_A \nu^{-1}$, and if $\sigma \in W$, then

$$\beta_{\nu A,\nu\chi}(\nu\sigma\nu^{-1}) = (\nu\chi)(\nu\sigma\nu^{-1})\theta((\nu\upsilon)^{-1}\nu\sigma\nu^{-1}\nu\upsilon) = \chi(\sigma)\theta(\upsilon^{-1}\sigma\upsilon) = \beta_{A,\chi}(\sigma).$$

In particular, $\beta_{A,\chi} = 1$ on W_A if and only if $\beta_{\nu A,\nu\chi} = 1$ on $W_{\nu A}$. Therefore if $a \in T_{\lambda;\chi,\theta}$, then $\hat{\nu}(a) \in T_{\lambda;\nu\chi,\theta}$, and if $a \in T_{\lambda;\nu\chi,\theta}$, then $\hat{\nu}^{-1}(a) = \widehat{\nu^{-1}}(a) \in T_{\lambda;\chi,\theta}$, and we are done.
By substituting $\theta = 1_{S_\lambda}$ in (9.1.1) we obtain

Corollary 9.1.2. *For any $\nu \in N$, any $\lambda \in S_\lambda$, and any $\chi \in X_W$ one has:*
(i) the automorphism $\hat{\nu} \in Aut_0(T_{d;W})$ maps the set $T_{\lambda;\chi}$ of all χ-orbits onto the set $T_{\lambda;\nu\chi}$ of all $\nu\chi$-orbits;
(ii) if $(1^d) \in D$, the hidden automorphism $\alpha \in Aut_0^{h;W'}(T_{D;W})$ maps the set $T_{\lambda;\chi}$ of all χ-orbits in $T_{D;W}$ onto the set $T_{\lambda;\alpha\chi}$ of all $\alpha\chi$-orbits in $T_{D;W}$.

Corollary 9.1.3. *For any $\nu \in N$, $\lambda \in P_d$, $\chi \in X_W$, and $\theta \in X_{S_\lambda}$, one has:*
(i) $n_{\lambda;\nu\chi,\theta} = n_{\lambda;\chi,\theta}$ and $n_{\lambda;\nu\chi} = n_{\lambda;\chi}$;
(ii) if $(1^d) \in D$, then for any hidden automorphism $\alpha \in Aut_0^{h;W'}(T_{D;W})$ one has $n_{\lambda;\alpha\chi,\theta} = n_{\lambda;\chi,\theta}$ and $n_{\lambda;\alpha\chi} = n_{\lambda;\chi}$.

Taking into account (9.1.3), (i), (5.2.4), (i), (iv), and [8, Ch. I, Sec. 7, 7.3], we establish

Corollary 9.1.4. *(i) For any $\nu \in N$, and any $\chi \in X_W$ the induced monomial representations $Ind_W^{S_d}(\chi)$ and $Ind_W^{S_d}(\nu\chi)$ of the symmetric group S_d, are equivalent;*
(ii) if $(1^d) \in D$, then for any hidden automorphism $\alpha \in Aut_0^{h;W'}(T_{D;W})$ the induced monomial representations $Ind_W^{S_d}(\chi)$ and $Ind_W^{S_d}(\alpha\chi)$ of the symmetric group S_d, are equivalent.

9.2. Let $a, b \in T_{\lambda;W}$, $\lambda \in P_d$, and let $\chi \in X_W$, $\theta \in X_{S_\lambda}$. It is said that the pair of characters (χ, θ) *separates a from b* if $a \in T_{\lambda;\chi,\theta}$ and $b \notin T_{\lambda;\chi,\theta}$. The character $\chi \in X_W$ *separates a from b* if $a \in T_{\lambda;\chi}$ and $b \notin T_{\lambda;\chi}$. We say that a and b are *indistinguishable via pairs of characters* if: (a$_{PC}$) a and b are contained in one and the same G''-orbit, and (b$_{PC}$) for any pair of characters (χ, θ) that separates a from b there exists a permutation $\nu \in N'$ such that $(\nu\chi, \theta)$ separates b from a, and for any pair of characters (χ, θ) that separates b from a there exists a permutation $\nu \in N'$ such that $(\nu\chi, \theta)$ separates a from b.
It is said that a and b are *indistinguishable via characters* if: (a$_C$) a and b are contained in one and the same G''-orbit, and (b$_C$) for any character $\chi \in X_W$ that separates a from b there exists a permutation $\nu \in N'$ such that $\nu\chi$ separates b from a, and for any character $\chi \in X_W$ that separates b from a there exists a permutation $\nu \in N'$ such that $\nu\chi$ separates a from b.
Otherwise, a and b are said to be *distinguishable via pairs of characters*, respectively, *via characters*.
By setting $\theta = 1_{S_\lambda}$ we obtain that if a and b are indistinguishable via pairs of characters, then a and b are indistinguishable via characters.

Theorem 9.2.1. *The members of a chiral pair are indistinguishable via pairs of characters.*

Proof: Let $a' \in T_{\lambda;W'}$ be a chiral pair, that is, $\psi^{-1}(a') = \{a, a_1\}$, $a, a_1 \in T_{\lambda;W}$, $a \neq a_1$. In compliance with Lunn-Senior's thesis 1.5.1, (2b), a and a_1 are contained in one and the same G''-orbit. Corollary 8.2.4 yields that the chiral involution $\hat{\tau} \in Aut_0^{h;W'}(T_{d;W})$ permutes a and a_1. Now, suppose that the pair of characters (χ, θ) separates a from a_1, so $a \in T_{\lambda;\chi,\theta}$ and $a_1 \notin T_{\lambda;\chi,\theta}$. Then in compliance with Theorem 9.1.1, (i), $\hat{\tau}(T_{\lambda;\chi,\theta}) = T_{\lambda;\tau\chi,\theta}$. Therefore $a_1 \in T_{\lambda;\tau\chi,\theta}$ and $a \notin T_{\lambda;\tau\chi,\theta}$, so the pair $((\tau\chi, \theta)$ separates a_1 from a. Thus, a and a_1 are not distinguishable via pairs of characters.

Corollary 9.2.2. *The members of a chiral pair are indistinguishable via characters.*

10.1. In this Subsection our constant reference is 6.4. We remind that the group G of univalent substitution isomerism of ethene C_2H_4 is the Klein four group $G = \{(1), (12)(34), (13)(24), (14)(23)\}$ in S_4. There are no chiral pairs among the derivatives of ethene, so $G = G'$, and hence the group $Aut'_0(T_{4;G})$ of chiral automorphisms coincides with the group $Aut_0(T_{4;G})$.
Here is the complete diagram:

$$T_{4;G}:$$

$$
\begin{array}{cccccccccc}
(4) & & & & & a_{(4)} & & & & \\
\downarrow & & & & & \downarrow & & & & \\
(3,1) & & & & & a_{(3,1)} & & & & \\
\downarrow & & & & \swarrow & \downarrow & \searrow & & & \\
(2^2) & & & & a_{(2^2)}\leftrightarrow & b_{(2^2)} & c_{(2^2)} & & & \\
\downarrow & & & \swarrow & & \downarrow & & \searrow & & \\
(2,1^2) & & a_{(2,1^2)} & & \leftrightarrow & b_{(2,1^2)} & & c_{(2,1^2)} & & \\
\downarrow & & * & & & * & & * & & \\
(1^4) & a_{(1^4)} & & & b_{(1^4)}\leftrightarrow & c_{(1^4)} & e_{(1^4)}\leftrightarrow & f_{(1^4)} & & h_{(1^4)} \\
 & \nwarrow & - & - - - & - & - - - & - & - & \nearrow &
\end{array}
$$

The horizontal double arrow means that the two diamers are identical as structural isomers. The star $*$ below a structural formula indicates that all possible arrows from it to any structural formula from the next row are drawn.
Plainly, any automorphism α from $Aut_0(T_{4;G})$ leaves invariant the elements $a_{(4)}$ and $a_{(3,1)}$, and if, for instance, $\alpha(a_{(2^2)}) = b_{(2^2)}$, then $\alpha(a_{(2,1^2)}) = b_{(2,1^2)}$. Similarly, if for example, $\alpha(a_{(2^2)}) = a_{(2^2)}$, then $\alpha(a_{(2,1^2)}) = a_{(2,1^2)}$, etc. On the six letters $a_{(1^4)}$, $b_{(1^4)}$, $c_{(1^4)}$, $e_{(1^4)}$, $f_{(1^4)}$, $h_{(1^4)}$, there are no restrictions on α. Thus, we have proved

Theorem 10.1.1. *One has*

$$Aut_0(T_{4;G}) \simeq S_3 \times S_6,$$

where the permutations of S_3 simultaneously move the elements a, b, c with indices (2^2) and $(2,1^2)$, and S_6 consists of all permutations of the six elements with indices (1^4).

We have $N = N' = S_4$, so in accord to Corollary 8.2.3 there are $|N/G| = 6$ hidden symmetries in $Aut_0(T_{4;G})$, and we obtain

Proposition 10.1.2. *The group $Aut_0^h(T_{4;G})$ of hidden symmetries of ethene consists of the unit permutation, and*

$$\widehat{(12)} = (b_{(2^2)}\ c_{(2^2)})(b_{(2,1^2)}\ c_{(2,1^2)})(a_{(1^4)}\ b_{(1^4)})(c_{(1^4)}\ e_{(1^4)})(f_{(1^4)}\ h_{(1^4)}),$$

$$\widehat{(23)} = (a_{(2^2)}\ c_{(2^2)})(a_{(2,1^2)}\ c_{(2,1^2)})(a_{(1^4)}\ e_{(1^4)})(b_{(1^4)}\ f_{(1^4)})(c_{(1^4)}\ h_{(1^4)}),$$

$$\widehat{(13)} = (a_{(2^2)}\ b_{(2^2)})(a_{(2,1^2)}\ b_{(2,1^2)})(a_{(1^4)}\ h_{(1^4)})(b_{(1^4)}\ c_{(1^4)})(e_{(1^4)}\ f_{(1^4)}),$$

$$\widehat{(123)} = (a_{(2^2)}\ b_{(2^2)}\ c_{(2^2)})(a_{(2,1^2)}\ b_{(2,1^2)}\ c_{(2,1^2)})(a_{(1^4)}\ c_{(1^4)}\ f_{(1^4)})(b_{(1^4)}\ h_{(1^4)}\ e_{(1^4)}),$$

$$\widehat{(124)} = (a_{(2^2)}\ c_{(2^2)}\ b_{(2^2)})(a_{(2,1^2)}\ c_{(2,1^2)}\ b_{(2,1^2)})(a_{(1^4)}\ f_{(1^4)}\ c_{(1^4)})(b_{(1^4)}\ e_{(1^4)}\ h_{(1^4)}).$$

This yields

COROLLARY 10.1.3. *The diamers of ethene in the pairs* $\{a_{(2^2)}, b_{(2^2)}\}$, $\{a_{(2,1^2)}, b_{(2,1^2)}\}$, $\{a_{(1^4)}, h_{(1^4)}\}$, $\{b_{(1^4)}, c_{(1^4)}\}$, $\{e_{(1^4)}, f_{(1^4)}\}$ *are indistinguishable via substitution reactions.*

PROOF: Proposition 10.1.2 implies that the permutation

$$\widehat{(13)} = (a_{(2^2)}, b_{(2^2)})(a_{(2,1^2)}, b_{(2,1^2)})(a_{(1^4)}, h_{(1^4)})(b_{(1^4)}, c_{(1^4)})(e_{(1^4)}, f_{(1^4)})$$

is an element of the group $Aut_0^h(T_{4;G}) \leq Aut_0'(T_{4;G})$, and, moreover, in agreement with the consideration in [7, VI] and in 6.4, the diamers in the above pairs are structurally identical.

The Abelian group X_G of one-dimensional characters of the group G consists of the unit character, and the characters χ_1, χ_2, and χ_3, defined in 6.4. The normalizer $N = S_4$ acts on X_G and the unit character is one of the orbits of this action. The other orbit is

$$\{\chi_1, \chi_2, \chi_3\},$$

because $\widehat{(123)}\chi_1 = \chi_2$, and $\widehat{(123)}\chi_2 = \chi_3$.
On the other hand, the Abelian group $X_{S_{(2^2)}}$ of one-dimensional characters of the group $S_{(2^2)} = \langle (12), (34) \rangle$ has four elements: the unit character θ_0, and the characters θ_1, θ_2, and θ_3, defined by the equalities

$$\theta_1((12)) = 1,\ \theta_1((34)) = -1,$$
$$\theta_2((12)) = -1,\ \theta_2((34)) = 1,$$

and

$$\theta_3((12)) = -1,\ \theta_3((34)) = -1.$$

The propositions below, together with (10.1.3), confirms the conclusions in [7, VI], and in 6.4.

PROPOSITION 10.1.4. *The members of the diameric pairs* $\{a_{(2^2)}, b_{(2^2)}\}$, $\{a_{(2,1^2)}, b_{(2,1^2)}\}$, $\{a_{(1^4)}, h_{(1^4)}\}$, $\{b_{(1^4)}, c_{(1^4)}\}$, $\{e_{(1^4)}, f_{(1^4)}\}$ *cannot be distinguished via pairs of characters.*

PROOF: In compliance with 5.1 and 6.4, we obtain

$$a_{(2^2)} \notin T_{(2^2);\chi_1,\theta_0},\ b_{(2^2)} \notin T_{(2^2);\chi_1,\theta_0},\ a_{(2^2)} \in T_{(2^2);\chi_2,\theta_0},\ b_{(2^2)} \notin T_{(2^2);\chi_2,\theta_0},$$
$$a_{(2^2)} \notin T_{(2^2);\chi_3,\theta_0},\ b_{(2^2)} \in T_{(2^2);\chi_3,\theta_0},$$

$$a_{(2^2)} \in T_{(2^2);\chi_1,\theta_1},\ b_{(2^2)} \in T_{(2^2);\chi_1,\theta_1},\ a_{(2^2)} \notin T_{(2^2);\chi_2,\theta_1},\ b_{(2^2)} \in T_{(2^2);\chi_2,\theta_1},$$
$$a_{(2^2)} \in T_{(2^2);\chi_3,\theta_1},\ b_{(2^2)} \notin T_{(2^2);\chi_3,\theta_1},$$

$$a_{(2^2)} \in T_{(2^2);\chi_1,\theta_2},\ b_{(2^2)} \in T_{(2^2);\chi_1,\theta_2},\ a_{(2^2)} \notin T_{(2^2);\chi_2,\theta_2},\ b_{(2^2)} \in T_{(2^2);\chi_2,\theta_2},$$
$$a_{(2^2)} \in T_{(2^2);\chi_3,\theta_2},\ b_{(2^2)} \notin T_{(2^2);\chi_3,\theta_2},$$

$$a_{(2^2)} \notin T_{(2^2);\chi_1,\theta_3},\ b_{(2^2)} \notin T_{(2^2);\chi_1,\theta_3},\ a_{(2^2)} \in T_{(2^2);\chi_2,\theta_3},\ b_{(2^2)} \notin T_{(2^2);\chi_2,\theta_3},$$
$$a_{(2^2)} \notin T_{(2^2);\chi_3,\theta_3},\ b_{(2^2)} \in T_{(2^2);\chi_3,\theta_3},$$

so we get the statement about the (2^2)-pair. The statements about the $(2, 1^2)$- and (1^4)-pairs are obvious because the stabilizers of any representatives of these G-orbits are trivial.

Corollary 10.1.5. *The members of the diameric pairs* $\{a_{(2^2)}, b_{(2^2)}\}$, $\{a_{(2,1^2)}, b_{(2,1^2)}\}$, $\{a_{(1^4)}, h_{(1^4)}\}$, $\{b_{(1^4)}, c_{(1^4)}\}$, $\{e_{(1^4)}, f_{(1^4)}\}$ *cannot be distinguished via characters.*

10.2. The group G of benzene C_6H_6 is defined up to conjugation in [7, IV] (see also [2]) and has order 12. We know from the experiment that there are no chiral pairs among the products of benzene and this conclusion is confirmed by the Lunn-Senior's model with the fact that there are no groups G' of order 24 that contain G (see [7, V]) . Therefore $G = G'$ and $Aut_0'(T_{D;G}) = Aut_0(T_{D;G})$ for any $D \subset P_6$. The classical Körner relations among the di- and tri-substitution homogeneous derivatives (see 7, I) yield immediately

Theorem 10.2.1. *If* $D = \{(4,2), (3^2)\}$, *then the group* $Aut_0'(T_{D;G})$ *is the unit group.*

Corollary 10.2.2. *The di-substituted (para, ortho, and meta), and tri-substituted (asymmetric, vicinal, and symmetric) derivatives of benzene are distinguishable via the Körner genetic relations.*

Remark 10.2.3. In [5], it is shown that the same is true for any organic compound whose molecule can be divided into a skeleton and six univalent substituents, and such that it has one mono-substitution and at least three di-substitution homogeneous derivatives, and, moreover, has a group G of univalent substitution isomerism of order 12.

10.3. The groups G and G' of univalent substitution isomerism and stereoisomerism, respectively, of cyclopropane C_3H_6 are found up to conjugation in [7, V], and in [4], and have orders 6 and 12, respectively. Moreover, the group G is dihedral. We set

$$D = \{(6), (5,1), (4,2), (4,1^2), (3^2)\}.$$

The possible substitution reactions among the products with empirical formula in D are represented in the tables below (see [5, Section 5] up to notation).

Zooms of $T_{D;G}$:

$$\begin{array}{c} (6) \\ \downarrow \\ (5,1) \\ \downarrow \\ (4,2) \end{array} \qquad \begin{array}{c} a_{(6)} \\ \downarrow \\ a_{(5,1)} \\ * \\ a_{(4,2)} \quad b_{(4,2)} \qquad c_{(4,2)} \quad e_{(4,2)} \end{array} \tag{10.3.1}$$

$$\begin{array}{c} (4,2) \\ \downarrow \\ (3^2) \end{array} \quad \begin{array}{ccc} & a_{(4,2)} & \\ \swarrow & & \downarrow \\ b_{(3^2)} & & c_{(3^2)} \end{array} \quad \begin{array}{ccc} & b_{(4,2)} & \\ \swarrow & & \downarrow \\ c_{(3^2)} & & a_{(3^2)} \end{array} \quad \begin{array}{ccc} & c_{(4,2)} & \\ \swarrow & & \downarrow \\ a_{(3^2)} & & b_{(3^2)} \end{array} \tag{10.3.2}$$

$$\begin{array}{c} (4,2) \\ \downarrow \\ (3^2) \end{array} \qquad \begin{array}{c} e_{(4,2)} \\ * \\ a_{(3^2)} \quad b_{(3^2)} \qquad c_{(3^2)} \quad e_{(3^2)} \end{array} \tag{10.3.3}$$

$$\begin{array}{c} (4,2) \\ \downarrow \\ (4,1^2) \end{array} \quad \begin{array}{c} a_{(4,2)} \\ \downarrow \\ a_{(4,1^2)} \end{array} \quad \begin{array}{c} b_{(4,2)} \\ \downarrow \\ b_{(4,1^2)} \end{array} \quad \begin{array}{c} c_{(4,2)} \\ \downarrow \\ c_{(4,1^2)} \end{array} \quad \begin{array}{ccc} & e_{(4,2)} & \\ \swarrow & & \downarrow \\ e_{(4,1^2)} & & f_{(4,1^2)} \end{array} \tag{10.3.4}$$

The G'-orbits are

$$a_{(4,2)} \cup b_{(4,2)},\ c_{(4,2)},\ e_{(4,2)},$$

$$a_{(3^2)} \cup b_{(3^2)},\ c_{(3^2)},\ e_{(3^2)},$$

$$a_{(4,1^2)} \cup b_{(4,1^2)},\ c_{(4,1^2)},\ e_{(4,1^2)} \cup f_{(4,1^2)}.$$

In particular, the pairs $\{a_{(4,2)}, b_{(4,2)}\}$, $\{a_{(3^2)}, b_{(3^2)}\}$, $\{a_{(4,1^2)}, b_{(4,1^2)}\}$, $\{e_{(4,1^2)}, f_{(4,1^2)}\}$, are chiral.

THEOREM 10.3.5. *(i) One has*

$$Aut_0(T_{D;G}) \simeq S_3 \times S_2,$$

where the permutations of S_3 simultaneously move the elements a, b, c with indices $(4,2)$, (3^2), and $(4,1^2)$, and S_2 consists of all permutations of $e_{(4,1^2)}, f_{(4,1^2)}$;
(ii) one has

$$Aut'_0(T_{D;G}) \simeq S_2 \times S_2,$$

where the permutations of the first direct component S_2 simultaneously move the elements a, b with indices $(4,2)$, (3^2), and $(4,1^2)$, and the second direct component S_2 consists of all permutations of $e_{(4,1^2)}, f_{(4,1^2)}$.

PROOF: Let $\alpha \in Aut_0(T_{D;G})$. In accordance with (10.3.1), $\alpha(a_{(6)}) = a_{(6)}$, $\alpha(a_{(5,1)}) = a_{(5,1)}$, and the diagrams (10.3.2) and (10.3.3) yield $\alpha(e_{(3^2)}) = e_{(3^2)}$ and $\alpha(e_{(4,2)}) = e_{(4,2)}$. The last equality together with (10.3.4) implies that the sets $\{e_{(4,1^2)}, f_{(4,1^2)}\}$, and $\{a_{(4,1^2)}, b_{(4,1^2)}, c_{(4,1^2)}\}$ are α-stable. Now, comparing (10.3.2) with (10.3.4), we get (i). Part (ii) can be obtained from (i) by taking into account that a chiral automorphism $\alpha \in Aut_0(T_{D;G})$ maps a chiral pair onto a chiral pair.

COROLLARY 10.3.6. *The products that correspond to the different sets of structural formulae below are distinguishable via substitution reactions among the elements of $T_{D;G}$:*

$$\{a_{(4,2)}, b_{(4,2)}\},\ \{c_{(4,2)}\},\ \{e_{(4,2)}\},$$

$$\{a_{(3^2)}, b_{(3^2)}\},\ \{c_{(3^2)}\},\ \{e_{(3^2)}\},$$

$$\{a_{(4,1^2)}, b_{(4,1^2)}\}\ \{c_{(4,1^2)}\},\ \{e_{(4,1^2)}, f_{(4,1^2)}\}.$$

The products that correspond to the members of a particular set are indistinguishable via substitution reactions.

PROOF: For the first statement, it is enough to note that all sets are $Aut'_0(T_{D;G})$-stable. Since all pairs are chiral, we get the second statement by using Theorem 8.2.6.

Theorem 2.1 and Section 5 from [5], and [4, 7.3.1] yield immediately

REMARK 10.3.7. All statements in this Subsection are true for any organic compound whose molecule can be divided into a skeleton and six univalent substituents, and such that it has one mono-substitution and at least three di-substitution homogeneous derivatives, and, moreover, has a group $G \leq S_6$ of univalent substitution isomerism of order 6, that is dihedral.

REMARK 10.3.8. The more precise definition of distinguishability of two compounds that includes chirality, Corollary 10.3.6, and Remark 10.3.7, specify the conclusions in [5, Section 5].

In [7, VII], the group G'' of structural isomerism of cyclopropane is described. In particular, the order of G'' is 48, and we have $G \leq G' \leq G''$. The G''-orbits in T_D are

$$a_{(6)},$$

$$a_{(5,1)},$$

$$a_{(4,2)} \cup b_{(4,2)} \cup e_{(4,2)}, \; c_{(4,2)},$$

$$a_{(3^2)} \cup b_{(3^2)}, \; c_{(3^2)} \cup e_{(3^2)},$$

$$a_{(4,1^2)} \cup b_{(4,1^2)} \cup e_{(4,1^2)} \cup f_{(4,1^2)}, \; c_{(4,1^2)}.$$

Therefore we obtain the next proposition which completes the description of the isomers of cyclopropane, considered in present Subsection.

Proposition 10.3.9. *The products of cyclopropane that correspond to the structural formulae within any one of the sets*

$$\{a_{(6)}\},$$

$$\{a_{(5,1)}\},$$

$$\{a_{(4,2)}, b_{(4,2)}, e_{(4,2)}\}, \; \{c_{(4,2)}\},$$

$$\{a_{(3^2)}, b_{(3^2)}\}, \; \{c_{(3^2)}, e_{(3^2)}\},$$

$$\{a_{(4,1^2)}, b_{(4,1^2)}, e_{(4,1^2)}, f_{(4,1^2)}\}, \; \{c_{(4,1^2)}\}$$

are structurally identical, and the products that correspond to members of different sets and have the same empirical formula, are structural isomers.

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